

# Development of a Corrosion Inhibitor for Reinforced Concrete

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Because of its highly alkaline concrete environment, reinforcing-steel surface is protected from corrosion by a thin oxide film. This film is maintained only in the absence of substances that form soluble complexes with iron. One of these substances is the chloride ion found in common deicing salt. Domtar Inc. established a research program to address the problem of rehabilitation of corroding reinforced-concrete structures. The experimental procedures and measuring techniques used to identify suitable corrosion inhibitors and typical results obtained with a selected inhibitor are presented. The inhibitor proved effective in reducing corrosion of steel embedded in concrete, and therefore it can be applied either as a curative or preventive means to protect reinforced-concrete structures.

In regions where winter brings snow and ice, both chemical and mechanical means are used to keep road surfaces clean and dry. The most popular deicing chemical is sodium chloride. Because it is a natural and abundant mineral, salt is economical. Difficulties arising from its use include its corrosiveness toward metals, particularly reinforcing steel in highway structures.

The widespread use of corrosion inhibitors in various situations suggested that a suitable inhibitor could be found to protect the reinforcing steel.

The purpose of this project was to find a chemical that, when added to deicing salt, would reduce the corrosion of the steel in reinforced-concrete structures. It was also hoped that in studying different inhibitors using a variety of experimental techniques it would be possible to determine the mechanism by which inhibitors can protect reinforcing-steel bars (rebars) in concrete.

The following selection criteria were established:

- The corrosion inhibitor must work in a concrete environment in which the pH is higher than 12, calcium hydroxide is present, and chlorides are often the aggressive ions;
- The corrosion inhibitor must work through concrete making the conditions favorable for the formation of a passive film;
- The corrosion inhibitor must retard further corrosion in actively corroding structures and minimize corrosion in new construction;
- The corrosion inhibitor must be a cost-effective solution to the problem of corrosion;
- The corrosion inhibitor must be environmentally acceptable;
- The corrosion inhibitor must be compatible with the materials that may come in contact with it. These include

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concrete, plastic, rubber, paint, and metals other than steel;

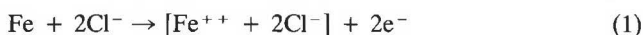
- The product must be readily available; and
- The corrosion inhibitor must not reduce the deicing effectiveness of salt.

Concrete normally provides an environment in which steel is passivated (1). A layer of  $\text{Fe}_2\text{O}_3$  is formed on the surface of steel, which protects it from further corrosion. One of concrete's protective mechanisms is the pH control action of calcium hydroxide crystals located at the steel-concrete interface. Yonezarva et al. (2) concluded that for the protective mechanism to operate, adhesion between the steel and the concrete is necessary because formation of voids at the steel-concrete interface is essential for active corrosion to start (2). Reduction of the pH by carbonates and attack by aggressive ions can destroy this passive layer and lead to active corrosion (3,4).

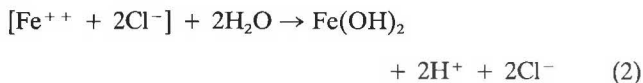
The corrosion products of steel occupy a volume about four times that of the steel itself. The forces created because of this increase in volume cause cracking of the concrete and delamination as shown in Figure 1.

Figure 2 is a schematic illustration of the corrosion of reinforced steel in concrete. Depassivation of the steel by anions such as chlorides, that migrate through the concrete pore network or through hairline cracks and structural cracks in the concrete, triggers the anodic dissolution of iron. A local corrosion cell is created sustaining iron oxidation and oxygen reduction, the two corrosion reactions.

In the presence of chloride ions, iron reacts to form an intermediate iron chloride complex, as indicated by Equation 1.



This complex reacts with moisture, as shown by Equation 2, to form ferrous hydroxide, and leaves chloride ions free to prevent further passive film formation (5).



## TESTING METHODOLOGY

### Testing a Corrosion Inhibitor for Reinforcement Steel

As a rule, a corrosion test simulates service conditions. Thus in the case of a corrosion inhibitor designed to reduce the corrosion of reinforcing steel in concrete, a test begins by

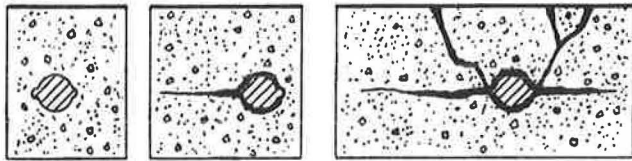


FIGURE 1 Cracking of concrete caused by the corrosion product of steel.

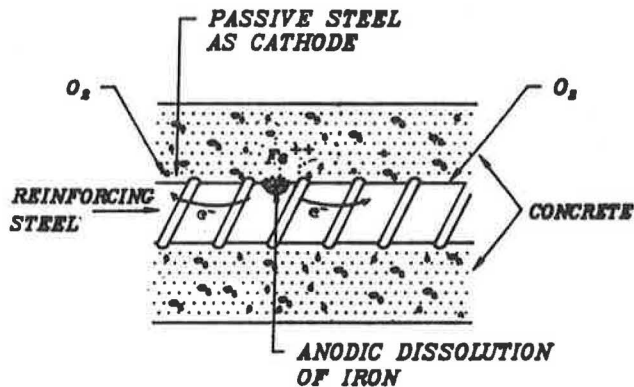


FIGURE 2 Schematic of corrosion of reinforcement steel in concrete.

simulating the chemical conditions in concrete, and progresses to the simulating of service conditions. The procedure includes the following:

- **Immersion Test.** A saturated calcium hydroxide solution containing sodium and potassium hydroxides simulates the concrete pore solution. Immersion of metal coupons in this solution is useful as a quick screening test because it does not require difficult specimen preparation and it allows for direct surface examination. However, it cannot be considered a sufficient test because it does not include all the limitations of a concrete cover.
- **Lollipop Test.** An embedded steel probe provides a closer simulation of service life conditions. The drawback of this procedure is the time required to prepare the specimens and the time required for the corrosion to start or to slow down (usually on the order of months). The results are also scattered and must be carefully interpreted.
- **Macrocell Test.** Specimens that create a macrocell effect to simulate service conditions must also be considered. This is also a time-consuming procedure and the results must be carefully interpreted.

A combination of these three testing procedures will give a realistic evaluation of corrosion inhibitor effectiveness.

### Measurement Techniques

Electrochemical measurement techniques are important for the following reasons: (a) the corrosion rate of reinforcement steel is not high in normal conditions, and (b) weight loss determination implies destruction of the specimen and does not explain the corrosion evolution. The following techniques

are best suited in this case because they are nondestructive; the last two in particular can measure corrosion rates down to low levels.

1. Half-cell potential measurements give qualitative evaluation of the corrosion state of the reinforcing steel. Because half-cell potential is a thermodynamic parameter, it gives the probability for corrosion to happen but not the rate at which it progresses.

2. Linear polarization gives a reasonable estimate of the corrosion rate, and various instruments for its measurement are available in standard laboratories. Correction must be made for concrete resistance.

3. Electrochemical impedance spectroscopy also gives a reasonable estimate of the corrosion rate; moreover, it also gives clues about the corrosion mechanism. For example, the corrosion rate is often temporarily limited by the oxygen diffusion through the concrete. This behavior immediately shows on the impedance diagram.

A combination of these techniques must be used to determine the effectiveness of a corrosion inhibitor as a function of time. A variety of other electrochemical techniques is also available. Each method has its advantages and disadvantages. The most widespread technique, as far as corrosion of steel in concrete is concerned, is the method of linear polarization with current interruption, which compensates for concrete resistance.

### Experimental Procedure

#### *Immersed Rebar Steel (Immersion Test)*

Steel samples were cut from one length of rebar, which is commonly used for construction. Initial sample preparation consisted of wet-grinding on SIC papers to a 600-grit (17- $\mu\text{m}$ ) finish, followed by a 3- $\mu\text{m}$  diamond-paste polish. Electrical connection was made by spot-welding a 0.15-mm-diameter Pt wire to each specimen. The unpolished surfaces of the samples were coated with Lacomit varnish to prevent exposure to the solutions. The contact area and a portion of the Pt wire were also coated. The solutions were prepared from reagent-grade chemicals and distilled, deionized water. The pore solutions were KOH (0.6 M) + NaOH (0.2 M) +  $\text{Ca}(\text{OH})_2$  (saturated). The NaCl concentrations were 0 and 0.52 M (3 percent by weight). The inhibitor concentration was  $\approx 2.5$  percent by weight of salt (0.074 percent by weight of solution). This last formulation, of salt plus the inhibitor, is named "TCI."

The electrochemical experiments were performed in beakers, open to air, containing  $\approx 200$  ml of solution. The counter electrode was a 6- $\text{cm}^2$  Pt foil and the reference electrode was a saturated calomel electrode (SCE). The corrosion current measurements were made manually on a daily basis. Linear polarization measurements were made by manually changing the potential in 2-mV steps to  $\pm 10$  mV to the measured corrosion potential and recording the current response. The polarization resistance was then calculated from the slope of the overvoltage-current plot. Alternatively, a triangular voltage perturbation (10 mV<sub>peak-to-peak</sub>) was applied at a sweep rate of 2.5 mHz, and the polarization resistance was calculated from the slope of the linear portion of the recorded curve.

Both of these methods gave similar results, and for most of the tests the manual technique was used. For the Tafel slope determination, anodic and cathodic scans of  $\pm 250$  mV were performed with a generator at a scan rate of 20 mV/min.

### Steel Embedded in Mortar (Lollipop Test)

Mortar specimens used in initial studies were cylinders of dimensions 50 mm (height)  $\times$  25 mm (diameter) as shown in Figure 3. The mortar mix design was 1 part portland cement, 1 part water, and 5 parts sand.

Rebars 70 mm in length and 11 mm in diameter were placed in the center of the mortar cylinder (one in each cylinder). Before placement, the top and bottom portions of each rebar were coated with wax to give a length of rebar exposed for 35 mm, or approximately an exposed surface area of 12 cm<sup>2</sup>. The concrete cover to the surface of the steel was 7 mm thick. The concrete probes were allowed to cure for 2 days in their molds, demolded, and immersed in deionized water where they were allowed to cure for 28 days.

Several electrochemical techniques were used in this study. Linear polarization, current transient decay, and electrochemical impedance spectroscopy are complementary methods that were used. For clarity of presentation, results of electrochemical impedance only will be reported because each method gave similar results. The constant used for corrosion rate determination was 26 mV. This value was found by Gonzalez et al. (6) to give, in most cases, an acceptable agreement between the gravimetric weight loss and that calculated from polarization resistance values.

Electrochemical measurements were made using a Solartron 1286 potentiostat/galvanostat and a Solartron 1250 frequency response analyzer controlled by a Hewlett-Packard 9816 computer. The experimental apparatus was configured using the three-electrode measurement system. The rebar

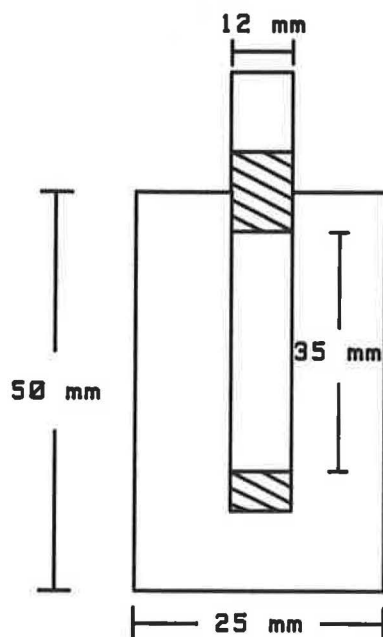


FIGURE 3 Schematic of a lollipop specimen.

specimen was used as the working electrode, a series of interconnected graphite rods as the counter electrode, and a saturated calomel electrode as the reference electrode.

### Simulated Macrocell

Small concrete slabs for laboratory-scale macrocell corrosion current measurements were built from construction-type rebars 11 mm in diameter, and concrete mix design in the proportions portland cement, 1.00; water, 0.52; sand, 1.76; and aggregate 2.36. The chloride concentration (as Cl<sup>-</sup>) was 9 kg/m<sup>3</sup> (15 lb/yd<sup>3</sup>), and the unit weight of concrete was 2,235 kg/m<sup>3</sup> (3,726 lb/yd<sup>3</sup>). This concrete mix design was used by FHWA to represent an average-quality concrete (7). (A lower ratio of water to cement and use of specialized admixture would significantly improve the concrete quality.)

Figure 4 is a schematic of the prism used in the laboratory-scale macrocell tests. The macrocell was a concrete block 9.5 cm (3 3/4 in.) high, 11.4 cm (4 1/2 in.) wide, and 22.9 cm (9 in.) long. The two mats of rebars were cast in the concrete prisms using average-quality air-entrained concrete. The concrete cover was 1.9 cm (3/4 in.) over the top mat of rebar. It was 1.3 cm (1/2 in.) over the lower mat of rebar to ensure good oxygen availability to the cathodic part of the macrocell. Sodium chloride was admixed into several of the top mat layers to accelerate corrosion and simulate the environment present in old bridge decks. A dam was placed on top of each slab and 6 percent solutions of deicer product or water were ponded to a depth of 1.9 cm (3/4 in.). Solutions were replenished every 2 weeks.

The top and bottom sets of rebars were electrically connected and an on-off switch in series with a 1.0-ohm resistor was installed between the two mats.

The corrosion current flowing between the top and bottom mats was measured as the voltage drop across the 1.0-ohm resistor with the switch in ON (normal) position, or directly using a Hokuto Denko Corporation zero-shunt ammeter.

## RESULTS OBTAINED WITH A SELECTED CORROSION INHIBITOR

### Immersed Rebar Steel (Immersion Test)

The corrosion rate measured by linear polarization of rebar steel specimens immersed in simulated pore solution for 65 days is shown in Figure 5. Curve 3 represents the behavior

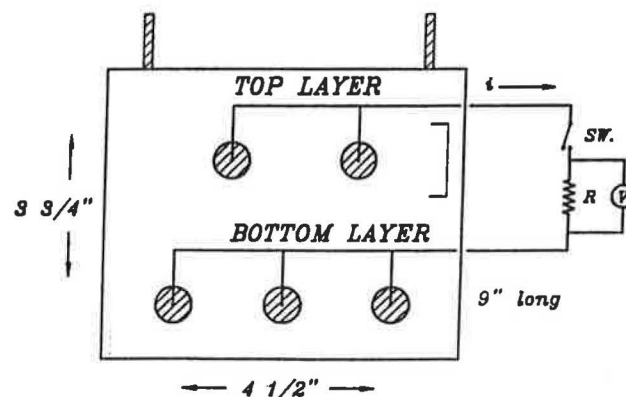


FIGURE 4 Schematic of a laboratory-scale macrocell.

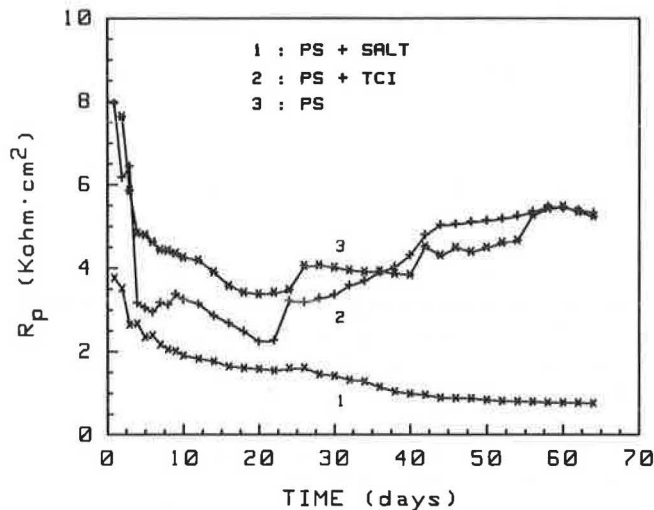


FIGURE 5 Polarization resistance of steel immersed in pore solution for 65 days.

of steel in pore solution without aggressive ions. The polarization resistance was high for all the experiments, indicating a low corrosion rate. The polarization resistance in the solution containing NaCl decreased (Curve 1), then stabilized at the lower level over the 60-day period. Curve 2 shows the polarization resistance in the presence of TCI. The measured polarization resistance was in the same range as in straight pore solution after 25 days, indicating a low corrosion rate. These results demonstrate the ability of the inhibitor to reduce the corrosion rate, even in the presence of chloride ions, to its background level in pore solution without aggressive ions.

#### Steel Embedded in Mortar (Lollipop Test)

A rebar steel specimen of known surface area was embedded in mortar. The mortar cover was made small to accelerate the diffusion through it and, therefore, to reduce the response time for aggressive ions or for the inhibitor to affect the embedded steel. The mortar can also be made with chloride admixture to simulate a contaminated reinforced-concrete structure.

Figure 6 shows the corrosion rate of embedded rebar probes in salt solutions with and without inhibitor. The measurements were made by electrochemical impedance spectroscopy. In the absence of the inhibitor, the corrosion rate increased dramatically, then stabilized after 2 months. With the inhibitor, the corrosion rate never attained such magnitude and was still decreasing after 3 months.

This case indicates the effectiveness of the corrosion inhibitor with steel embedded in mortar.

#### Simulated Macrocell

One important behavior of reinforced-steel structures is the formation of a macrocell. Iron oxidation and oxygen reduction, the two corrosion reactions, happen at different locations on the structure. Because of the origin of the chloride contamination (sodium chloride for deicing), a bridge deck will

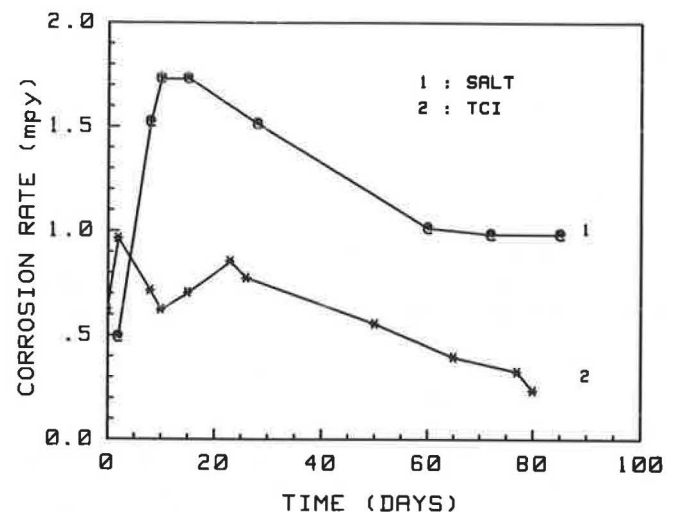


FIGURE 6 Corrosion rate of mortar lollipops.

often form a macrocell where the iron oxidation occurs at the top mat of rebars (high chloride concentration) and the oxygen reduction occurs at the lower mat of rebars (availability of oxygen is higher because of dryer conditions). A simulated macrocell can be built in the laboratory by making a concrete prism where the top layer is contaminated with chloride. A macrocell will be established, giving rise to a macrocell current.

A total of 16 specimens were used in this study. The results with three slabs, for which the top layer of concrete was not contaminated with salt, are shown in Figure 7. The slabs were ponded with 6 percent NaCl solutions with and without inhibitor, and with distilled water only. At first, the current increased for the three slabs. After this initiation period, the slab containing the inhibitor showed a sharp decrease in current down to almost zero. With the brine solution only, the current slowed down but still stayed relatively high, indicating a well-established corrosion rate. Visual examination of the concrete specimens revealed extensive cracking in the absence of inhib-

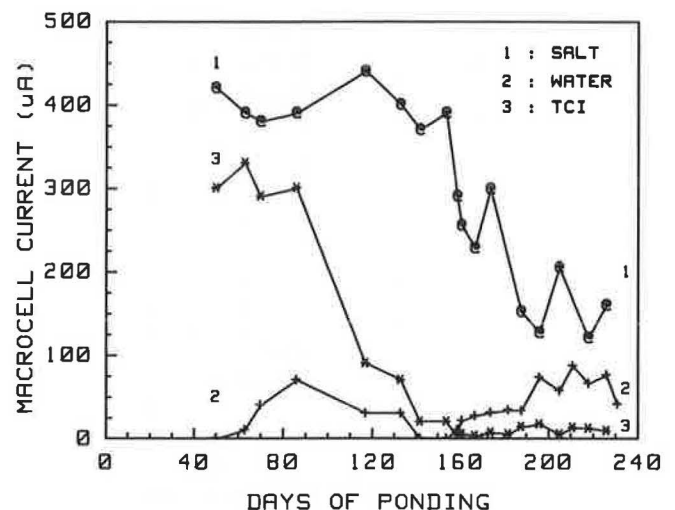


FIGURE 7 Macrocell current obtained with three slabs not contaminated with NaCl and ponded for 8 months.

itor. The slab ponded with water only had a small macrocell current, indicating little corrosion, as expected for a concrete specimen not contaminated with chloride ions.

A similar behavior was observed with a chloride-contaminated specimen as shown in Figure 8. After 5 months of ponding with the inhibitor in solution, the macrocell current was reduced to low values. The prism ponded with brine solution and with water only exhibited a high current throughout the experiment. This behavior was expected, because the concrete was contaminated with chloride ions at fabrication of the specimens. The break at 170 days happened when the electrical contacts of all the cells were redone, cleaned, and reassembled. The reduction in the macrocell current observed with the inhibitor proves its effectiveness in already-contaminated concrete where active corrosion is taking place.

### Insight into the Mechanism

#### Passive Film Examination

Examination of the passive film on the steel surface indicated the mechanism by which this inhibitor can effectively reduce the corrosion of steel embedded in concrete. X-ray photoelectron spectroscopy (XPS) and scanning-electron microscopy (SEM) were used to investigate the surface chemistry and morphology. Steel specimens exposed to the simulated pore solution with TCI and parts of the rebar extracted from the TCI-treated slabs (macrocell test) were examined.

When the inhibitor was added to the pore solution, the surface morphology was different. Electron diffraction x-ray analysis indicated that the surface passive film was mainly

composed of calcium and iron. The XPS analysis revealed a common feature of the film formed in simulated pore solution with TCI and of the film found on the rebar in the TCI-treated slabs (macrocell test). The calcium regions on both samples indicate that there may be significant differences in the chemical species formed when the inhibitor is added to the system. These early results demonstrate that the inhibitor is effective through concrete. A full research program is continuing to determine the exact mechanism and its limitations.

#### Concrete Examination

SEM examination of the slabs ponded with TCI (macrocell test) indicated little effect on the concrete. Accumulation of the inhibitor near the surface of the slab was observed. Compared with the noninhibited specimens, insignificant amounts of iron diffused in the concrete around the rebar. The fibrous outgrowths on the calcium silicate hydrate crystal appeared unusually long in the TCI-treated specimen.

### CONCLUSION

The results demonstrate the ability of the inhibitor to eliminate most of the corrosive effect of chloride ions in a simulated concrete pore solution. Moreover, the corrosion inhibitor can work through concrete and create favorable conditions for the formation of a passive film on the reinforcing steel. Because this inhibitor can effectively reduce the corrosion rate of an already contaminated structure, it can be applied as a curative as well as a protective means for protecting reinforced concrete from corrosion.

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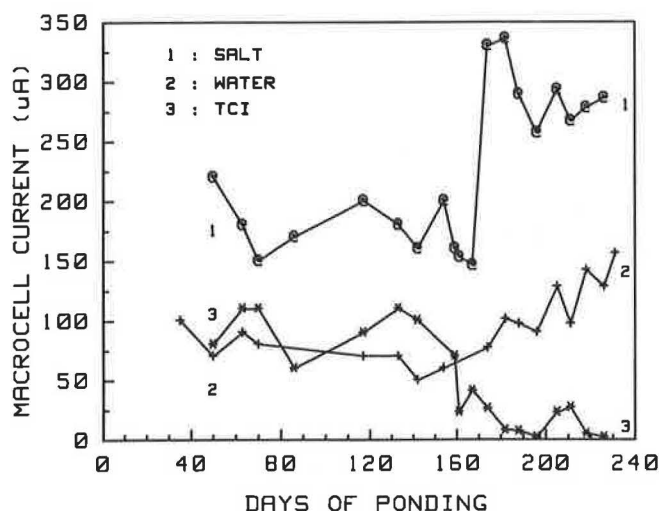


FIGURE 8 Macrocell current obtained with three slabs of which the top layer of concrete was contaminated with 15 lb/yd<sup>3</sup> of chloride and ponded for 8 months.